

THE HYDROPHOBIC CHARACTER OF PRETREATED COAL SURFACES

R. Jin, Y. Ye and J.D. Miller
Department of Metallurgy and Metallurgical Engineering
University of Utah, Salt Lake City, UT 84112

INTRODUCTION

In recent years, the production of superclean coal has been of considerable interest in order to partially replace oil and natural gas as fuel sources. Of all the coal-cleaning processes, flotation is one of the most versatile. Carbon dioxide coal flotation is a new technology developed at the University of Utah.⁽¹⁾ Compared with conventional flotation, carbon dioxide flotation enhances the ash rejection and increases flotation recovery for coals of different rank with the exception of lignite. However, significant improvement of the hydrophobicity and flotability of lignite has been found after controlled thermal pretreatment. The potential for the production of superclean coal by carbon dioxide has been demonstrated in bench scale flotation experiments.⁽²⁾

EXPERIMENTAL

Coal samples and experimental methods of flotation, contact angle measurement and bubble attachment time measurement have been described in a previous paper.⁽³⁾

In addition, a diffuse reflectance FTIR (DRIFT) technique has been used to characterize the coal surface.⁽³⁾ More recently, an attenuated total reflectance (ATR) accessory, the CIRCLE™ cell with a ZnSe rod from Spectra-Tech Inc., was used in ATR-FTIR spectroscopy. The coal for the ATR-FTIR analysis was ground to minus 1 micron in a ceramic mortar with distilled water at pH 6-6.5 before transferring to the CIRCLE™ cell at a coal/water ratio of 0.5 by weight. A spectrum for each coal was obtained by subtraction of water spectrum from the spectrum of the coal/water suspension. Both spectra were collected under the same conditions with the empty CIRCLE™ cell as a background.

XPS experiments were conducted with the Hewlett-Packard 5950 B instrument using monochromatic Al K_{α1,2} radiation at 1487 eV. Power at the X-ray source was 400 watts and the chamber vacuum was controlled at 10⁻¹⁰ torr. An electron gun at 6 eV supplied a flux of low-energy electrons to the coal surface to minimize heterogeneous charging artifacts in the resulting spectra.

RESULTS AND DISCUSSION

Coal Hydrophobicity

As shown in Figs. 1 and 2, it has been found by reagent-less Hallimond tube flotation and by contact angle and bubble attachment time measurements that the hydrophobicity and flotability of coals increase with an increase in coal rank, reaching a maximum for low-volatile bituminous coal and then decreasing with a further increase in coal rank. These traditional methods are excellent indicators of the macroscopic hydrophobicity of the coal surface. However, to better describe the hydrophobic/hydrophilic balance at a coal surface, it is important to establish the corresponding chemical characteristics of these coals.

DRIFT- and ATR-FTIR spectroscopy can provide a more detailed description of the coal surface than elemental bulk composition or chemically determined acid-group content as used by previous investigators.⁽⁴⁾ These two FTIR techniques have been used to evaluate the hydrophobicity of fine coals by a spectroscopic criterion--the hydrophilicity index--which contrasts the relative abundance of surface hydrophilic groups OH and COOH with the relative abundance of surface hydrophobic groups ArH and RH.⁽³⁾ Using the hydrophilicity index determined by both DRIFT- and ATR-FTIR spectroscopy, a rank-dependence of coal hydrophobicity can be plotted as shown in Fig. 2. Note that the hydrophobic character of coal estimated by the hydrophilicity index varies with coal rank in much the same fashion as bubble attachment time, contact angle, and flotation recovery. Since the coal rank is essentially classified by the carbon content, the hydrophilicity index determined by FTIR

spectroscopy is obviously a more detailed index for evaluating coal hydrophobicity than coal rank or carbon content.

To ensure the surface sensitivity of the FTIR techniques and confirm the conclusions reached from the FTIR analysis, XPS has also been used to evaluate the hydrophobic character of fine coals. The ratio C/O determined by XPS has also been used to define a hydrophobicity index for the coals. Such a hydrophobicity index for six coals of different rank is presented in Fig. 1. Notice that the rank-dependence of coal hydrophobicity estimated by XPS agrees with that evaluated by other methods such as FTIR spectroscopy, flotation response, contact angle and bubble attachment time measurements.

Enhanced Hydrophobicity of Pretreated Coal

Characterization of CO₂-treated coal

As shown in Table 1, it has been found that CO₂ pretreatment increases coal hydrophobicity. Table 2 indicates that enhanced hydrophobicity of CO₂-pretreated coals results in an increased flotation recovery and enhanced ash rejection for coals of different rank with the exception of lignite. It has also been found that coals of middle ranks such as high-, medium-, and low-volatile bituminous coals are most amenable to carbon dioxide coal flotation.⁽⁵⁾

Oxidation can result in a reduced hydrophobicity of CO₂-pretreated coals. Figure 3 illustrates that oxidation of a CO₂-pretreated low-volatile bituminous coal in air reduces the coal hydrophobicity and restores the original lower hydrophobic character after about 20 hours of oxidation. Fortunately, coal oxidation is a slow process. No significant loss in coal hydrophobicity was observed during the first couple hours which was long enough to complete flotation experiments.

The success of CO₂ coal flotation has been attributed to the coal's high adsorption potential for CO₂.⁽⁶⁾ It has been found by monitoring the OH absorption band using in-situ FTIR spectroscopy that pore water and hydration water in coal are displaced by CO₂ during pressure treatment, which results in enhanced coal hydrophobicity as shown in Fig. 4.

A model for carbon dioxide adsorption by coal is being considered, and a schematic drawing of the microstructure is shown in Fig. 5. This drawing represents a final state of the adsorption process, where all the pore water and hydration water have been replaced by CO₂. Before CO₂ pretreatment, the positions of CO₂ molecules in this drawing are predominantly occupied by H₂O molecules. Displacement of the H₂O molecules by CO₂ molecules during pressure treatment and CO₂ nanobubble formation at the coal surface on pressure release are believed to be responsible for the improved flotation performance.

Characterization of thermally-treated coal

It has been found that low-temperature thermal treatment significantly increases the hydrophobicity of lignite as suggested by FTIR hydrophilicity index determinations and confirmed by bubble attachment time measurements/flotation response (see Fig. 6). It is believed that the increased hydrophobicity of lignite is attributed to the removal of pore water, hydration water and some organic OH functional groups as well as the diffusion of volatile matter to the surface and the reorientation of surface functional groups. As shown in Table 2, it has been found that controlled thermal treatment can also increase the hydrophobicity of subbituminous coal and anthracite. Finally it should be noted that the thermal treatment improves the flotation separation of lignite from mineral matter.

SUMMARY

Increased hydrophobicity and hence the flotability of coals of different rank has been observed for CO₂ pretreatment and/or controlled thermal pretreatment. DRIFT- and ATR-FTIR and XPS techniques have been used to determine the surface chemical characteristics in order to evaluate coal hydrophobicity. These results agree very well with those determined by traditional methods. The enhanced hydrophobicity of CO₂-treated coal is attributed to the high specific affinity of coal for CO₂ which results in the displacement of pore water and hydration water by CO₂ and on pressure release leads to nanobubble formation at the coal surface in aqueous suspension. Increased hydrophobicity of

lignite by thermal treatment arises from the removal of pore water, hydration water and some organic OH functional groups as well as the diffusion of volatile matter to the surface and the reorientation of surface functional groups.

The financial support provided by the U.S. Department of Energy under Grant No. DE-FG22-85PC80530 is greatly acknowledged.

REFERENCES

1. Miller, J.D. and Misra, M., 1987. U.S. Patent No. 4,676,804.
2. Miller, J.D. and Misra, M., 1985. Coal Preparation, 2:69.
3. Jin, R., Ye, Y. and Miller, J.D., 1987. "Evaluation of coal hydrophobicity by diffuse reflectance FTIR spectroscopy," presented at the 8th National Convention of the Royal Australian Chemical Institute, Aug.24-28, and submitted to Colloids and Surfaces.
4. Miller, J.D., Laskowski, J.S. and Chang, S.S., 1983. Colloids and Surfaces, 8:137.
5. Miller, J.D., Jin, R., Ye, Y. and Sadowski, Z., 1987. "Carbon dioxide for fine coal flotation," Final Report to U.S. Department of Energy, Grant No. DE-FG22-85PC80530.
6. Jin, R., Ye, Y. and Miller, J.D., 1988. "Studies of carbon dioxide adsorption at the surface of coal by in-situ FTIR spectroscopy," presented at the 117th AIME Annual Meeting, Jan.25-28, Preprint No. 88-300, submitted to Fuel.

Table 1 Contact Angle and Bubble Attachment Time for Different Gas Bubbles on a Polished Surface of Low-Volatile Bituminous Coal

| Pressure Treatment Using Corresponding Gas Phase at 20 psi | Gas Phase of Bubbles | Contact Angle (degrees) | Bubble Attachment Time (ms) |
|--|-------------------------|----------------------------|-----------------------------------|
| Yes | Air | 49-52 | 170-190 |
| Yes | N ₂ | 50-51 | 140-160 |
| Yes | CO ₂ | 54-56 | 20-25 |
| No | Air | 47-49 | 180-200 |
| No | N ₂ | 50-51 | 170-190 |
| No | CO ₂ | 51-53 | 140-150 |

Table 2 Enhanced Hydrophobicity and Improved Flotation Performance of Pretreated Coals of Different Rank

| Coal Rank | Ratio of Attachment Times τ_{CO_2}/τ_{air} | Increased Flotation Recovery by CO ₂ Pretreatment | Enhanced Ash Rejection by CO ₂ Pretreatment | Increased Hydrophobicity by thermal Pretreatment | Enhanced Ash Rejection by thermal, Pretreatment |
|--------------|---|--|---|---|--|
| ANT | 0.70 | Yes | Yes | Yes | |
| LVB | 0.80 | Yes | Yes | No | |
| MVB | 0.69 | Yes | Yes | No | |
| HVB | 0.66 | Yes | Yes | No | |
| SUB | 1.0 | Yes | Yes | Yes | |
| LIG | 1.0 | No | No | Yes | Yes |

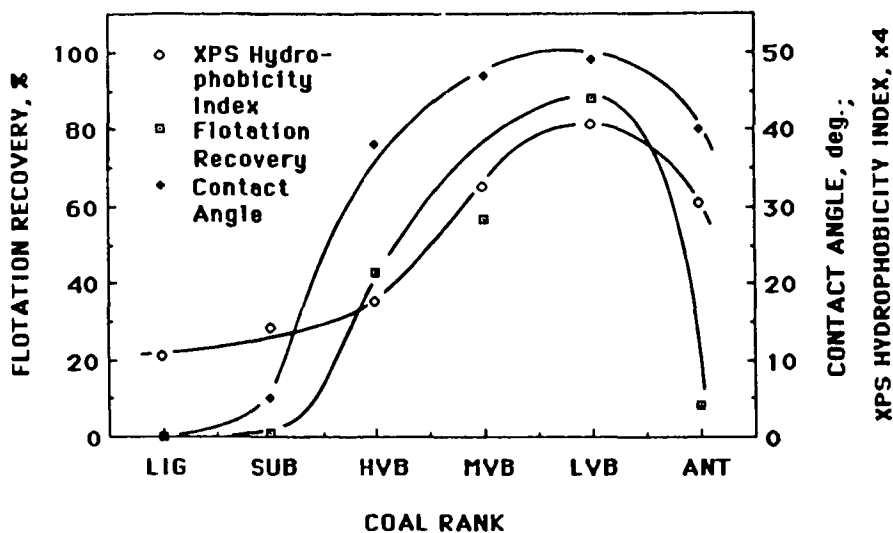


Figure 1 Coal hydrophobicity evaluated by Hallimond tube flotation, contact angle measurement, and XPS analysis as a function of coal rank. ANT = Anthracite, LVB = Low-volatile bituminous coal, MVB = Medium-volatile bituminous coal, HVB = High-volatile bituminous coal, SUB = Subbituminous coal, LIG = Lignite.

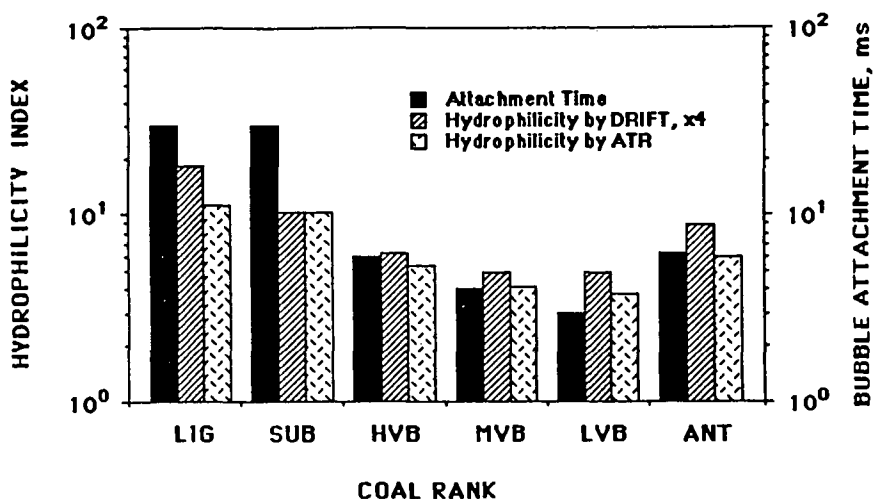


Figure 2 Hydrophobic character of coal as described by bubble attachment time and the hydrophilicity index determined from DRIFT- and ATR-FTIR spectra.

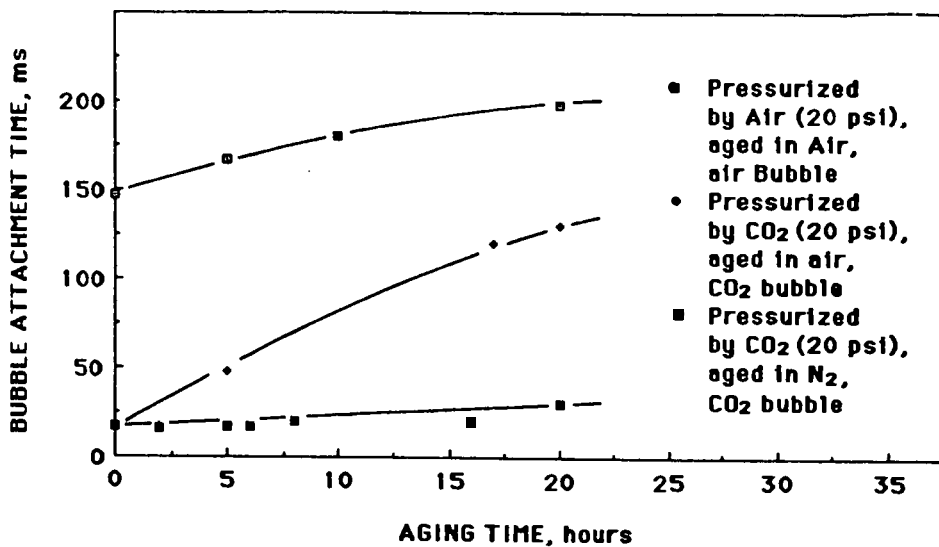


Figure 3 Bubble attachment time measured on the polished surface of a pretreated low-volatile bituminous coal as a function of aging time of the coal.

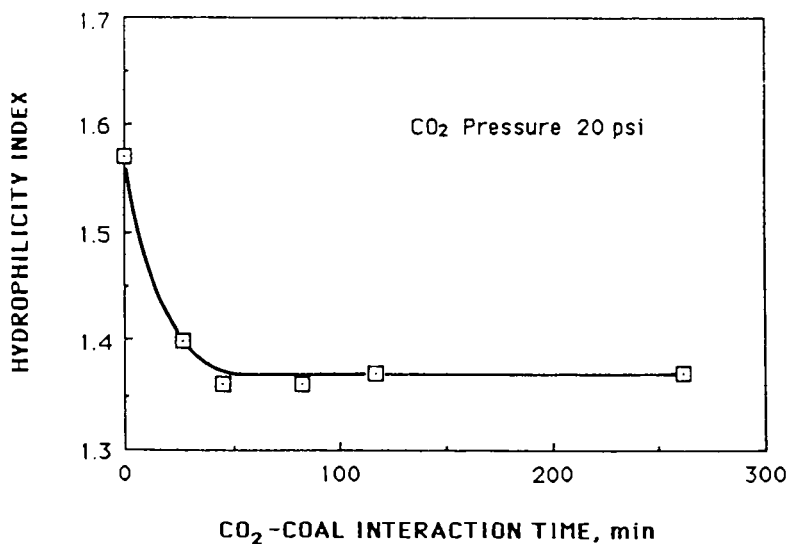


Figure 4 The hydrophilicity index of a CO₂-pretreated high-volatile bituminous coal (-5 micron) at 302 °K determined by DRIFT-FTIR spectroscopy as a function of CO₂-coal interaction time.

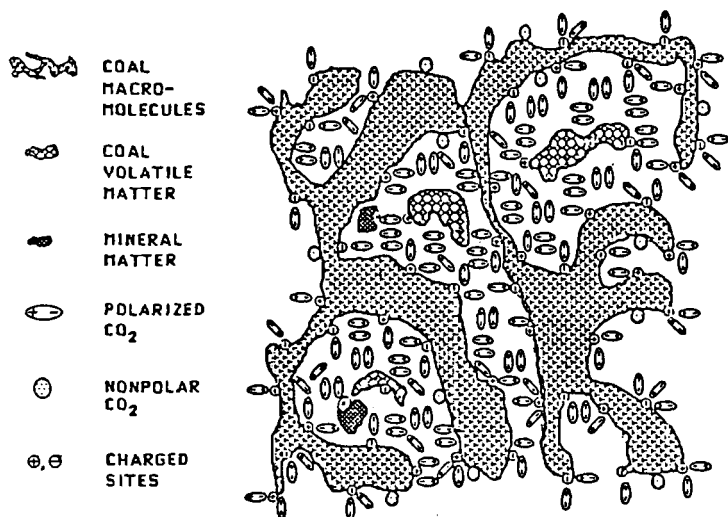


Figure 5 Schematic drawing of carbon dioxide adsorption by coal.

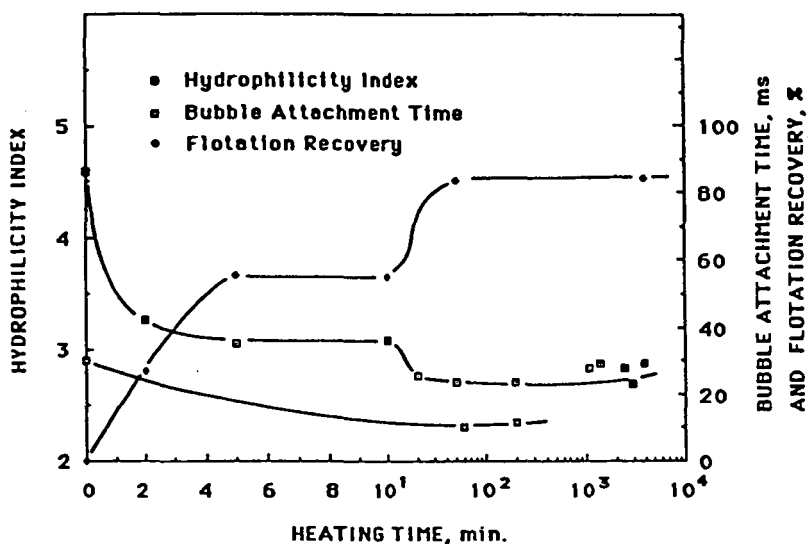


Figure 6 Hydrophobic character of lignite evaluated by the DRIFT-FTIR hydrophilicity index, bubble attachment time and flotation recovery as a function of thermal-treatment time.⁽³⁾